

Project HC-1: H-storage in nano-structured carbon-related materials and hydrides

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Since April 2003, for the purpose of developing new hydrogen storage materials with high-performance, the Hiroshima group has mainly studied the H-storage properties of (1) nano-structured graphite prepared by ball milling under high H₂-gas pressures up to 6 MPa, and (2) nano-composite Li-N-H system composed of the 1:1 mixture of lithium amide and lithium hydride prepared by ball milling at room temperature. The results obtained are summarized as follows:

(1) Effects of catalyst and milling pressure on H-storage in nano-structured graphite

We examined H-storage properties of graphite catalyzed by 3d-transition metals and mechanically milled graphite under hydrogen pressures ranging from 0.3 to 6.0 MPa at room temperature. The results indicated that a small amount of iron contamination from steel balls and milling vessel in the sample during milling process plays a quite important role as a catalyst for H-storage properties in graphite. The hydrogen concentration chemisorbed during 80 h milling decreases from 6.1 to 4.1 wt.% with increasing milling hydrogen pressure. The physisorption-like hydrogen concentration increases with increasing the milling hydrogen pressure and reaches more than 0.5 wt.% at 6 MPa. Moreover, higher pressure hydrogen suppressed the fracture rate of the milled graphite more effectively, suggesting that the hydrogen atoms trapped at the edges of the graphene sheets and at defective sites between the graphene layers near the surface are responsible for preserving the lamellar nanocrystalline structure, which may be the host for physisorption-like hydrogen absorption.

(2) H-storage properties in nano-composite Li-N-H system

We examined the basic properties in the 1:1 mixture of lithium amide (LiNH₂) and lithium hydride (LiH) as a candidate for reversible hydrogen storage. The thermal desorption mass spectra of the ball milled mixture without any catalysts indicated that hydrogen H₂ is released in temperature range from 180 to 400°C along with a considerable ammonia NH₃. On the other hand, the ball milled mixture containing a small amount of TiCl₃ as a catalyst showed the most superior hydrogen storage properties among the 1:1 mixtures containing a small amount of catalysts, Ni, Fe, Co metals and TiCl₃ (1 mol.%). That is, the product desorbs a large amount of hydrogen (~6 wt.%) in the temperature from 150 to 250°C at a heating rate of 5°C/min, but does not desorb ammonia at all within our experimental detectability. In addition, we confirmed that the product shows an excellent cycle retention, with effective hydrogen capacity of more than 5 wt.% and high reaction rate until at least 3 cycles.